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The Reaction between Phosphorus Pentoxide and Ammonia.

By Margot Becke-Goehring and Jürg Sambeth.

The reaction of P_4O_{10} with NH_3 proceeds by cleavage of the P_4O_{10} molecule. The main products are derivatives of di-phosphoric acid, which can be condensed at about $100^\circ C$, yielding an ammonium salt of polyphosphoric acid in which one half of the P-atoms are connected by O-bridges, the other half by NH-linkages.

The reaction between P_4O_{10} and NH_3 has been the subject of many investigations. Schiff ¹⁾, the earliest investigator, believed Phosphaminic Acid, $OP(NH)(OH)$, to be formed. Gladstone ²⁾, on the other hand, believed that he had obtained Diamidodiphosphoric acid, $P_2O_3(NH_2)_2(OH)_2$. According to Monte ³⁾ the reaction gives a mixture of ammonium diphosphates and ammonium metaphosphates and a product which can be described as an ammonium salt of a polyphosphoric acid in which the P-atoms are alternately linked by O- and NH-bridges respectively. Sanfourche, Hernette and Fau ⁴⁾ believed that by treatment of P_4O_{10} with NH_3 gas the diammonium salt of monoamidodiphosphoric acid, $P_2O_3(OH_4)_2(NH_2)(OH)$, was produced. Woodstock ⁵⁾ carried out the reaction between dry NH_3 and P_4O_{10} and heated the reaction mixture in the presence

1) H. Schiff, Liebigs Ann. Chem. 103, 168 (1857).

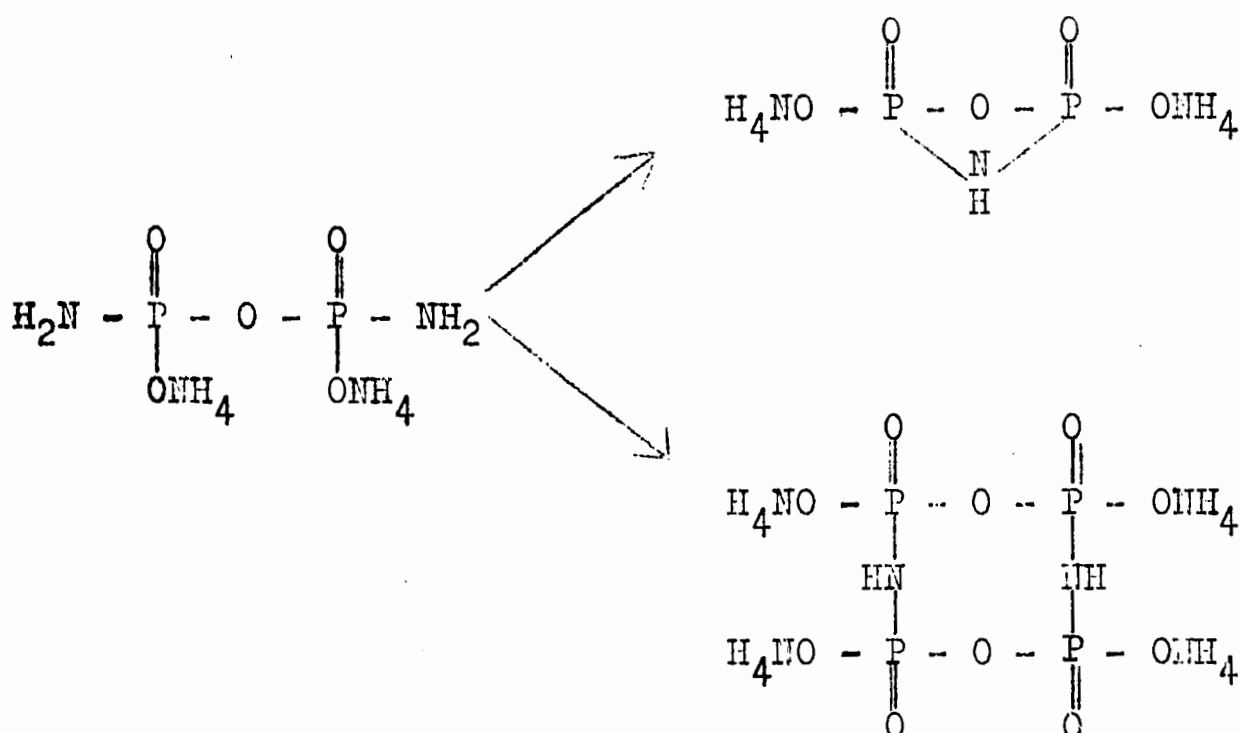
2) J. H. Gladstone, J. Chem. Soc. 21, 64 (1868).

3) A. Monte, Liebigs Ann. Chem. 248, 245 (1888).

4) A. Sanfourche, A. Hernette u. H. Fau, Bull. Soc. Chim. France [4] 47, 275 (1930).

5) W. H. Woodstock, U.S. Patent 2 122 122 v. 23.6.1938.

of dry NH_3 to at least 150°C . He thereby obtained products having a P:N ratio of less than 1.5:1. Woodstock also used liquid NH_3 as reactent, and yet other procedures, i.e. suspending the P_4O_{10} in an inert organic solvent through which he passed the gaseous NH_3 . He supposed the first product produced in this reaction to be the diammonium salt of diamidodiphosphoric acid, $\text{P}_2\text{O}_3(\text{ONH}_4)_2(\text{NH}_2)_2$, after which this was supposed to undergo condensation with formation of a 4- or 8-membered ring system.



Fischer ⁶⁾ obtained considerable confirmation of Woodstock's observations. However, he maintained that there was as yet no certain knowledge concerning the mechanism of reaction between P_4O_{10} and NH_3 .

This system appeared, therefore, to be a promising one for further study. We investigated the reaction of liquid NH_3 with P_4O_{10} and found that the substance underwent rapid reac-

⁶⁾ H. Fischer: Über die Reaktionsprodukte aus Phosphorpentoxyd und Ammoniak und deren Eignung zur Wasserenthärtung. Verlag M. Dittert u. Co., Dresden 1941.

tion, but that the surface of the P_4O_{10} soon became inaccessible to the NH_3 , thus bringing the reaction to a standstill. In a sealed tube it took about 5-6 weeks for completion of the reaction, when P_4O_{10} could no longer be detected on the X-ray diagram of the product ⁷⁾. However, the reaction can be carried out very rapidly in an autoclave, fitted with a magnetic stirrer, at temperatures between 40 and 50° C. In this way reaction was complete after 24 hrs. The atomic ration P:N: ammonium-N was 1:1.79:1.16. This ratio was also found by Fischer in some of his experiments ⁶⁾.

It was not possible to establish the homogeneity of this product. Chromatograms ⁸⁾ showed the presence of higher polymeric substances in the reaction product. 4 different spots were found, one of which could be monoamidophosphate, while the others were not characteristic of any known compounds containing P, N or O. On the other hand there was no trace of diamidophosphate.

A uniform product was obtained by heating the reaction product to temperatures between 100 and 110° C. Unlike Woodstock ⁵⁾ we carried out this heating under normal atmospheric conditions for several hours. NH_3 is liberated and the substance becomes puffed up to give a solid product, having an atomic ratio of P:N:Ammonium-N = 1:1.5:1.06.

This product is a light-grey powder, which dissolves slowly in cold water, but rather quickly when it is heated. The solution has an almost neutral reaction and coagulates albumen in acetic acid solution instantaneously. Chromatograms showed the presence of polyphosphate and of oligophosphate, the latter being supposedly obtained by hydrolysis of the polyphosphate.

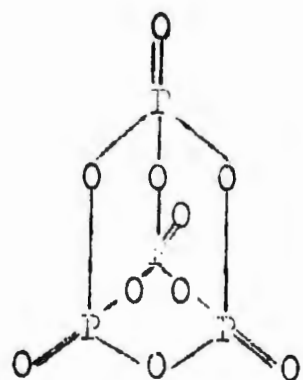
⁷⁾ Experiments of Dr.K.Niedenzu.

⁸⁾ G.Biberacher, Z.,anorg.allg.Chem. 285, 86 (1956).

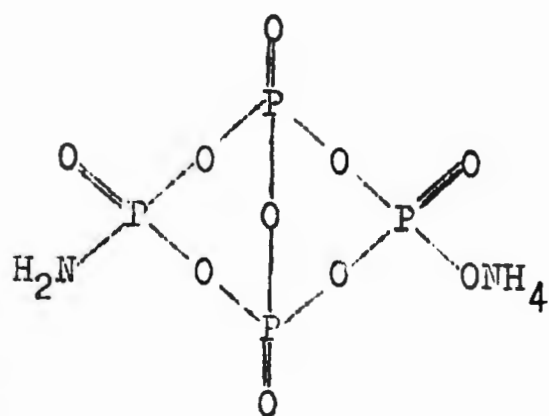
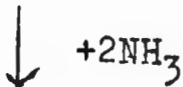
Solutions of our reaction product in water prove to have considerable ability to bind Ca. The binding was complete with an atomic ration of Ca:P = 1:5.4.

We should like to interpret the reaction as follows: P_4O_{10} normally is shown by the formula I ⁹⁾. It is supposed that firstly the compound II is formed by ammonolysis, while further reaction could yield either III or IV. Thilo and co-workers ¹⁰⁾ have shown by the solvolysis of P_4O_{10} with a polar solvent e.g. water derivatives of tetrametaphosphoric acid are mainly obtained. On the other hand one obtains derivatives of isotetrametaphosphoric acid (IV) when for example ether is used. On these grounds III is proposed as the principle product in the reaction between NH_3 and P_4O_{10} . It is fairly certain, that the compound IV was not obtained since this should split to give diamidophosphate besides other substances. We did not find this substance in any of our experiments, however. Since the compound III is also liable to undergo further reaction after a while it is possible that we obtained the compound V in the manner shown. Indeed Nieldenzu showed that this compound can be obtained when the reaction was carried out slowly at room temperature.

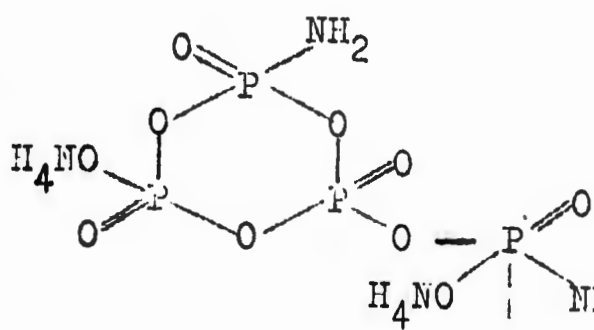
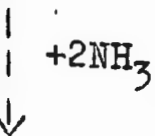
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- 9) B.Raistrick, Sci.J.Roy.Coll.Si. XIX, 9 (1949);
 H.J.Rodionowa u. Ju.W.Chodakow, J.allg.Chem.(UdSSR) 20,
 (82) 1347 (1950);
 R.N.Bell, W.F.Audrieth u. O.F.Hill, Ind.Eng.Chem. 44, 570
 (1952);
 R.Rätz u. E.Thilo, Liebigs Ann.Chem. 572, 173 (1951);
 E.Thilo u. H.Woggon, Z.anorg.allg.Chem. 277, 17 (1954).
 10) E.Thilo u. W.Wieker, Z.anorg.allg.Chem. 277, 27 (1954).



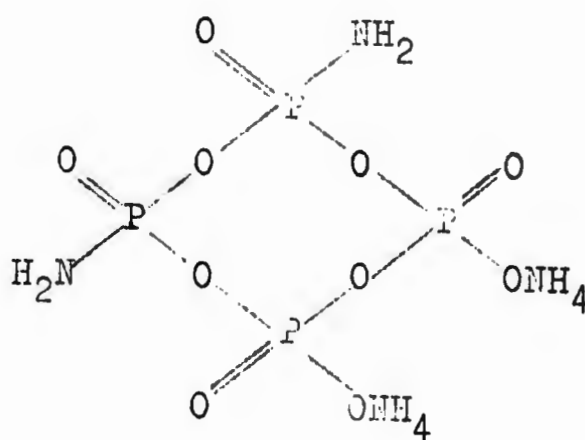
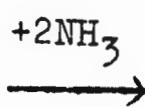
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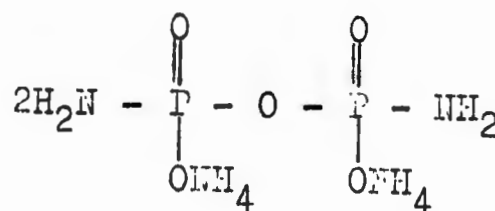
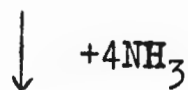
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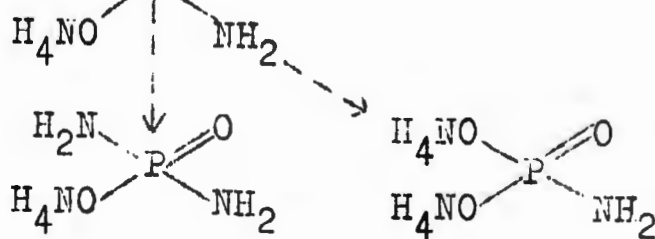
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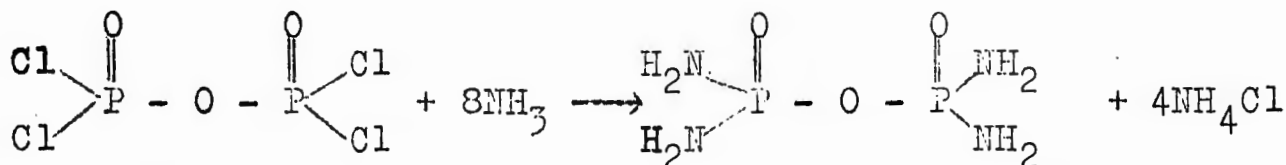
III



V



The ammonolysis does not go farther than this, as we have shown ¹¹⁾ that the ammonolysis of $P_2O_3Cl_4$ gives $P_2O_3(NH_2)_4$,

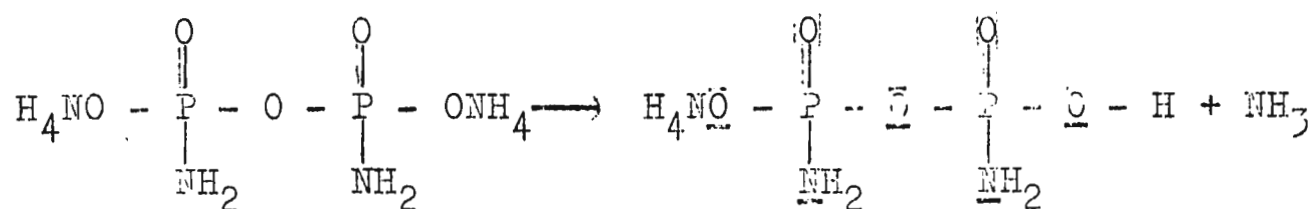


and no derivatives of orthophosphoric acid were produced.

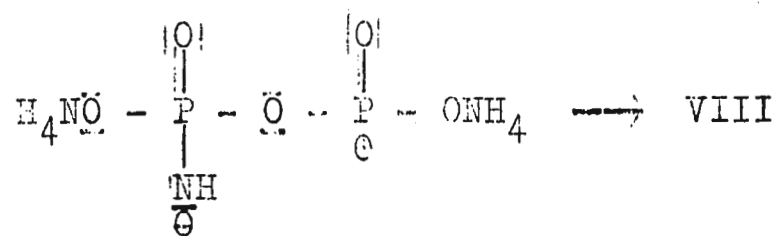
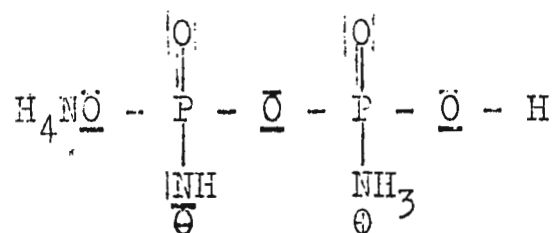
Thus, from the reaction between P_4O_{10} and liquid NH_3 a mixture of reaction products was obtained, which, we believe, include the compounds III and V. On heating this reaction product, condensation occur with simultaneous cleavage of NH_3 , as the final product shows an atomic ratio of P:N:Ammonium-N of about 1:1.5:1. This latter reaction can occur by either an intra- or intermolecular process. In the first case the reaction may be depicted as follows: the ammonium salt of diamidodiphosphoric acid (VI) is formed, after which rearrangement take place analogous to a reaction which has been previously described for amidophosphoric acid ¹²⁾. This substance will polymerize to a product (VIII) in which each P-atom is connected with 4 ligands.

11) M.Goehring u. K.Niedenzu, Chem. Ber. 89, 17 (1956).

12) H.Goehring u. J.Sambeth, Chem. Ber. 90, 232 (1957).

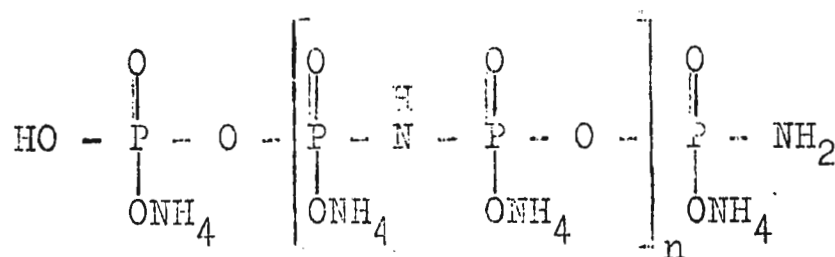


VI

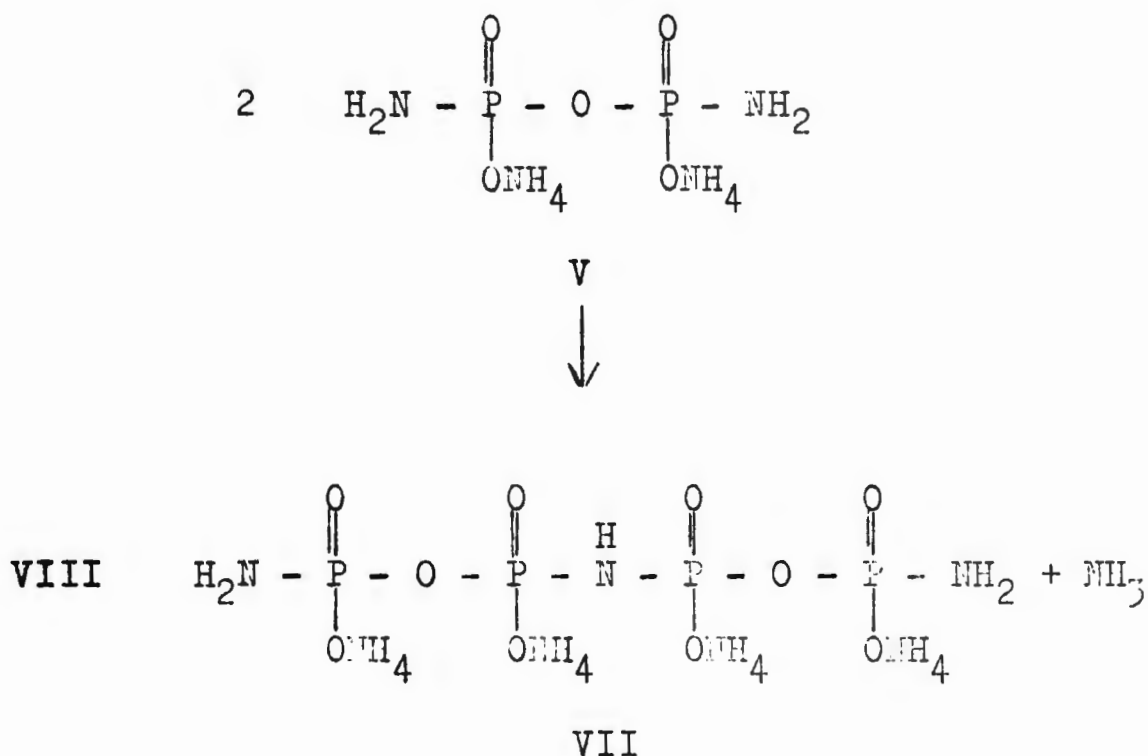


VIIIa

→ VIII



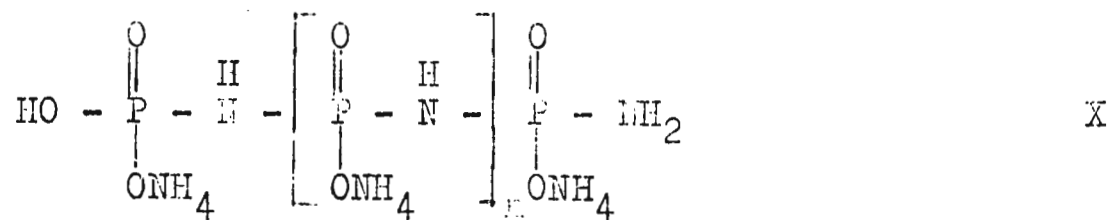
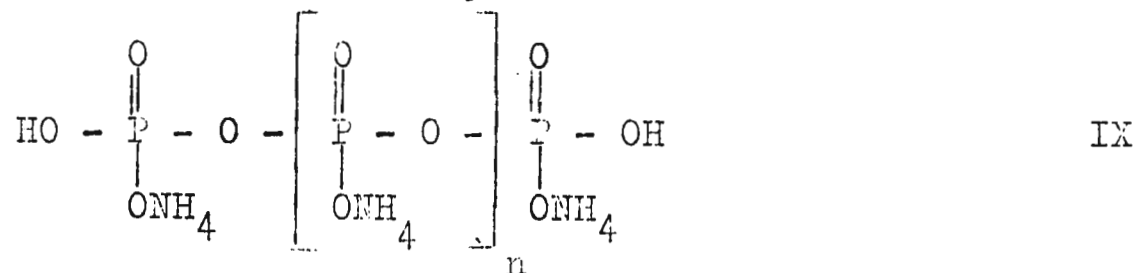
In the case of an intermolecular process the condensation will occur between 2 molecules of the diammonium salt of diamidodiphosphoric acid to give firstly a derivative of an imido-tetraphosphoric acid (VII), which will be able to take part in further condensation reactions. This reaction would be analogous to the behaviour of triamidophosphoric acid towards reagents which react with cleavage of NH_3 ¹³⁾:



In both cases an ammonium salt of a polyphosphoric acid is obtained, the P-atoms of which will be linked by O-bridges as well as by NH-bridges. It is quite understandable that this ammonium salt has a great ability to bind calcium. For an ammonium polyphosphate (IX), which is obtained by the rearrangement of amidophosphoric acid ¹²⁾, as well as an ammonium polyphosphate, obtained by the analogous rearrangement of diamidophosphoric acid both have the ability to bind Ca. The substance (VIII) therefore should possess the properties of both IX and X.

¹³⁾ H. Goehring u. K. Niedenzu, Chem. Ber. 89, 1771 (1956).

In fact the ability to bind Ca is as great with VIII as with IX. The analytical data proves the end product to have the given formula VIII. n should be about 1-4, the chromatograms showing more probability for n=4.



Experimental data

For the preparation of diammonium diamidodiphosphate⁷⁾ dry NH_3 is condensed on freshly sublimed P_4O_{10} in a thick walled tube; the NH_3 level should be at least 4 cm above the P_4O_{10} . The tube then is sealed and left at room temperature for 5-6 weeks. After opening the tube the NH_3 allowed to evaporate through solid KOH. Later the last traces are removed by heating in a water bath. The reaction product is then dried over P_4O_{10} in a vacuum desiccator for 24 hrs. and analysed directly, since the substance is very hygroscopic.

Analyses: Calc. P 29,5 N 26,7 Ammonium-N 13,3

Found P 29,6 N 26,5 Ammonium-N 13,3

The reaction of P_4O_{10} with NH_3 . A sufficient amount of liquid NH_3 is put into the reaction vessel of a 50 ml autoclave which is fitted with a magnetic stirrer. A small quantity of P_4O_{10} is put into the vessel and vigorous stirring begun at once. The autoclave is heated with continuous stirring at $40-50^\circ \text{C}$ for about 24 hrs. During this time, the reaction mixture becomes harder and harder, so that stirring becomes increasingly more difficult. After removal of the surplus NH_3 the autoclave is opened and the reaction mixture removed. The substance is powdered and put into a desiccator. It is a dark glass-like substance which has a grey, granular appearance when powdered.

The appearance does not change when dried in desiccator under high vacuum at 20°C for 10 hrs. It is not completely soluble in cold water, but dissolves easily however in hot water with a weakly acid reaction. The X-ray diagram shows very weak interferences of P_4O_{10} . The analyses of three different samples are the following:

P 29,9	N 23,4	Amm.-N 15,2	P:N:Amm.-N = 1 : 1,76 : 1,14
P 32,8	N 24,2	Amm.-N 15,5	P:N:Amm.-N = 1 : 1,63 : 1,05
P 29,7	N 24,2	Amm.-N 15,5	P:N:Amm.-N = 1 : 1,79 : 1,16

The greater amount of the substance is heated in an electric oven at 100-110° C for about 10 hrs. The smell of NH₃ which is noticed at the beginning disappears slowly, while the reaction product becomes puffed by this process, it retains its original appearance, and amorphous traces of P₄O₁₀ only being occasionally detected on the X-ray diagram. It produces immediate conglutination of albumen in acetic acid solution. The aqueous solution contains small metallic particles produced from the magnetic stirrer of the autoclave probably, but never more than 0,07 %.

Found P 30,9 N 20,5 Amm.-N 14,8

Calculated for the monomeric substance (VIIIa):

P 32,1 N 21,8 Amm.-N 14,5

Calculated für (VIII) with n=4 and chain ends saturated with water residue:

P 31,5 N 21,4 Amm.-N 14,3

The possibility of binding Ca has been investigated according to K.R. Andress und K. Wüst ¹⁴⁾. The binding was complete for an atomic ration of Ca : P = 1 : 5,4.

For the preparation of ammonium polyphosphinate an amount of diamidophosphoric acid is heated at 100-110° C in an electric oven. After 2-3 hrs. a glassy colourless substance is obtained, which is very hygroscopic and very soluble in water. The p_H of an 0,1 % solution is 7,69 at 20° C, while the p_H of the starting material is 3,55 under the same conditions. Unlike the starting

¹⁴⁾ K.R. Andress u. K. Wüst, Z.anorg.allg.Chem. 237, 120 (1933)

material the product obtained after the rearrangement is amorphous. The solution in water coagulates albumen in acetic acid solution instantaneously. The chromatogram⁸⁾ of the rearranged substance cannot be used as proof of its degree of polymerization.

The analyses are as follows:

Calc. N 29,2 Amm.-N 14,6

Found N 28,5 Amm.-N 13,7.

for the isomeric starting material, diamidophosphoric acid:

Calc. P 32,2 N 29,2 Amm.-N 0,0

Found P 32,1 N 28,6 Amm.-N 0,6.

The possibility of binding Ca has been investigated under the same conditions as described earlier for ammoniumpolyphosphate¹²⁾. The binding was accomplished with an atomic ration of Ca : P = 1 : 10,2.